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(54) **NONAQUEOUS ELECTROLYTE SECONDARY BATTERY**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte secondary battery capable of suppressing an internal pressure of a battery to a low level in the case where the battery is left at high temperature without deteriorating battery characteristics such as a battery capacity and high rate charge/discharge characteristics.

SOLUTION: In a nonaqueous electrolyte secondary battery provided with a positive electrode including mainly a lithium containing transition metal oxide an oxide selected from among SrOCaOBaO and MgO is disposed in the form of a solid such as powder or a molding inside a battery system in such a manner as not to be directly brought into contact with the electrode and an electrolyte and a carbon dioxide produced inside the battery is reacted with the above oxide to produce carbonate thus preventing any increase in the internal pressure of the battery.

CLAIMS

[Claim(s)]

[Claim 1] An anode which makes a lithium containing transition metal oxide a subject.
A negative electrode which uses lithium as an active material.
Nonaqueous electrolyte.

It is the nonaqueous electrolyte secondary battery provided with the above. It has arranged so that an electrode and an electrolysis solution may not carry out direct contact of at least one oxide chosen from a group of SrOCaOBaO and MgO which react to the carbon dioxide emitted in a fuel cell subsystem and can generate carbonate in the state of solid such as powder or a molding body.

[Claim 2] The nonaqueous electrolyte secondary battery according to claim 1 which made

an addition of an oxide 0.04 millimols - 0.20 millimol per 1 g of positive active material.
[Claim 3]The nonaqueous electrolyte secondary battery according to claim 1 which set an oxide to SrO.

[Claim 4]The nonaqueous electrolyte secondary battery according to claim 1 which a lithium containing transition metal oxide made $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (however either $\text{M}=\text{CoAl}$ or Mn or B is used and referred to as $0 \leq x \leq 0.3$).

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to improvement of the high temperature conservation characteristic of a nonaqueous electrolyte secondary battery.

[0002]

[Description of the Prior Art]In recent years portable-izing of electronic equipment and cordless making are progressing quickly and requests on the small size which bears these power supplies for a drive and the cell which is lightweight and has high energy density are mounting. From such a viewpoint as a nonaqueous secondary battery and a cell by which a rechargeable lithium-ion battery especially has high tension and high energy density it results in the existence which replaces the nickel-cadmium battery or nickel hydride battery of an alkaline aqueous solution system which occupied the mainstream till then centering on a notebook computer a cellular phone AV equipment etc. and big growth continues to be expected.

[0003]Now as for the rechargeable lithium-ion battery put in practical use the fuel cell subsystem using the carbon material which carries out occlusion of the lithium to a negative electrode or for which lithium containing transition metal oxide such as LiCoO_2 may be emitted to positive active material is marketed. In such a fuel cell subsystem a lithium ion deintercalates from an anode at the time of charge and a charge reaction is completed by intercalating into carbon which is a negative electrode. A reaction contrary to a charge reaction advances and a discharge reaction completes discharge because the lithium ion deintercalates from the carbon negative electrode returns into positive active material. When positive active material is $\text{Li}_{1-x}\text{CoO}_2$ (however referred to as $0 \leq x \leq 1.0$) the number of reaction electrons of the lithium which can be deintercalated at the time of charge is about $x = 0.5$ electrons and if it converts into the amount of anode specific volume it will become about 130 mAh/g. However since LiCoO_2 is in a 4.3V vs. Li/Li^+ grade and high potential in the state of full charge and lithium of $x = 0.5$ is deintercalated the crystal structure is in a very unstable state. When the cell of such a charging state is neglected to an elevated temperature (45 °C - about 85 °C) the characteristic degradation of positive active material not only happens but disassembling the organic solvent in an electrolysis solution and being accompanied by the generation of gassing it is liable to be known.

[0004]Generally with a rechargeable lithium-ion battery when inter cell pressure exceeds a fixed value for the safety reservation at the time of overcharge the security apparatus established in the obturation board operates and the safe structure of intercepting the current from the outside is used in many cases. However when the above cells are

neglected to an elevated temperature and gas is emitted so much the security apparatus may operate and the function as a cell may be lost. Then in order to reconcile the safety reservation at the time of the reliability in elevated-temperature neglect of a cell and overcharge it is required that the security apparatus which operates with the internal pressure of the fixed range established in the obturation board should be controlled strictly. On the other hand the trial which controls the gas yield in elevated-temperature neglect to the minimum is made the physical properties of the positive electrode material were controlled and using an electrolysis solution with good reducing reactivity and withstand voltage characteristic has been proposed.

[0005] Some of LiNiO_2 and nickel elements recently as positive active material which replaces LiCoO_2 towards the further high-capacity-izing of a rechargeable lithium-ion battery. Other elements for example the solid solution replaced by CoA or Mn or B is proposed (for example refer to JP6-60887A) and the development is progressing. Since the lithium volume which can be deintercalated at the time of charge is large and the amount of specific volume of 180 mAh/g - 200 mAh/g is obtained the expectation of LiNiO_2 is great but. In a charging state a crystal structure is still more unstable than LiCoO_2 and since it is liable to control the generation of gas at the time of elevated-temperature neglect is needed further.

[0006]

[Problem(s) to be Solved by the Invention] As mentioned above when elevated-temperature neglect of the nonaqueous electrolyte secondary battery which used the lithium containing transition metal oxide for positive active material is carried out by a charging state inter cell pressure may go up by the generation of gas accompanying disassembly of an electrolysis solution and the fault of intercepting current by the operation of a security apparatus may happen. In order to avoid this the material physical properties of positive active material were controlled and the trial which reduces the specific surface area of a granular material and an electrode and the trial which chooses an electrolysis solution with little generation of gas were carried out. However if such measures are taken many cases will bring about the fall of cell capacity the fall of a high charging and discharging characteristic etc. and will become difficult [it / to pull out a satisfying battery characteristic].

[0007] Then this invention solves the above problems and it aims at providing the nonaqueous electrolyte secondary battery which controls low the inter cell pressure at the time of carrying out elevated-temperature neglect of the cell without spoiling battery characteristics such as cell capacity and a high charging and discharging characteristic.

[0008]

[Means for Solving the Problem] In a nonaqueous electrolyte secondary battery provided with an anode in which this invention makes a lithium containing transition metal oxide a subject in order to solve the above-mentioned technical problem a negative electrode which uses lithium as an active material and nonaqueous electrolyte is considered as a nonaqueous electrolyte secondary battery arranged so that an electrode and an electrolysis solution may not carry out direct contact of at least one oxide chosen from a group of SrO , CaO , BaO and MgO which react to the gas emitted in a fuel cell subsystem and can generate carbonate in the state of solid such as powder or a molding body.

[0009] According to this invention when a cell of a charging state is neglected by elevated

temperature it becomes possible to control a rise of inter cell pressure by gas emitted by disassembly of an electrolysis solution and an added oxide reacting and lessening gas. [0010] In order to prevent a rise of inter cell pressure by the generation of gas at the time of elevated-temperature neglect without causing a fall of a battery characteristic it is effective to prevent a rise of inter cell pressure by absorbing emitted gas before the security apparatus in an obturation board operates.

[0011] Then as a result of conducting a component analysis of the gas first emitted it solved that most ingredients of gas were carbon dioxide. It solved that gas volume which originates in an anode as a source of release was dominant, when a cell was neglected at 85 °C as a gas yield gas volume increased in proportion to time a gas yield became about 1 l/h from several hours in about 10 hours and it turned out more that it does not generate. So in this invention a reaction is gently caused with carbon dioxide and suppose that it installs in a fuel cell subsystem so that a cell and an electrolysis solution may not carry out direct contact of the material which does not have an adverse effect on battery capacity.

[0012] As a result it finds out that an effect of this invention is acquired by adding at least one oxide in a group of SrOCaOBaO and MgO as an oxide which generates carbonate.

[0013] Although improving the cycle characteristic of a cell by adding at least one or more kinds of oxides chosen from BaOMgO and CaO and mixing with an active material in an anode is indicated by JP7-153496A this invention does not add in an anode at least one oxide chosen from SrOBaOMgO and CaO and is not mixed. It arranges so that direct contact of an electrode and the electrolysis solution may not be carried out in the state of solid such as powder or a molding body and both technical problems completely differ therefore arrangement forms of an oxide also differ.

[0014] Since these oxides react to carbon dioxide gently generate carbonate and exist stably within a fuel cell subsystem they do not cause a fall of battery capacity. About safety reservation at the time of overcharge described previously priority is given over the generation of gas by disassembly of an electrolysis solution at the time of overcharge oxygen evolution by disassembly of the positive active material itself happens and the reaction velocity is overwhelmingly quick compared with generation-of-gas speed at the time of elevated-temperature neglect. Therefore since inter cell pressure will go up and the security apparatus will operate safety to a surcharge is secured.

[0015]

[Embodiment of the Invention] Can carry out this invention with the gestalt indicated to each claim and like a statement to claim 1 In the nonaqueous electrolyte secondary battery provided with the anode which makes a lithium containing transition metal oxide a subject the negative electrode which uses lithium as an active material and nonaqueous electrolyte By arranging so that an electrode and an electrolysis solution may not carry out direct contact of at least one oxide chosen from the group of SrOCaOBaO and MgO which react to the carbon dioxide emitted in a fuel cell subsystem and can generate carbonate in the state of solid such as powder or a molding body When these oxides exist in a fuel cell subsystem apart from an anode negative electrode and an electrolysis solution it reacts to the carbon dioxide emitted when elevated-temperature neglect of the cell is carried out. When SrO is taken for an example it reacts to carbon dioxide and SrCO_3 is generated. Generated SrCO_3 is inertness comparatively exists stably within a fuel cell subsystem and does not have an adverse effect on a subsequent battery characteristic.

[0016]These oxides are the easiest to usually arrange at the pars basilaris ossis occipitalis of an obturation board. When an example is given as a configuration method there are the method of arranging at the pars basilaris ossis occipitalis in an obturation board with the gestalt of a solid such as molding an oxide into powder or a pellet type or mixing oxide powder with a binder and a solvent and applying on a metallic foil drying and welding of an obturation board etc. Of course as a configuration method it is not restricted to these and which method may be used if direct contact is not carried out to an electrode and an electrolysis solution.

[0017]It is good to make into 0.04 millimols - 0.20 millimol quantity of the oxide according to claim 2 added like per 1 g of positive active material.

[0018]That is as for the quantity of the oxide to add since it depends for the quantity of the carbon dioxide emitted at the time of elevated-temperature neglect of a cell on the quantity of the positive active material with which it fills up it is preferred that they are 0.04 millimols - 0.20 millimol per 1 g of positive active material. They are 0.06 millimols - 0.15 millimol more preferably. In less than 0.04 millimol the effect of this invention is not fully acquired and inter cell pressure cannot be controlled appropriately. On the other hand it becomes difficult to arrange in the fuel cell subsystem which the volume which an oxide occupies becomes large and in which it has only the limited volume of voids when 0.20 millimol is exceeded and the direction of the speed of the inter-cell-pressure rise by the volume of voids having decreased becomes quick and is not more preferred than a gas absorption reaction.

[0019]It is good to set to SrO the oxide according to claim 3 added like. That is the absorbance of carbon dioxide has very large SrO and it is because it is the most desirable as an oxide used for this invention since the reactivity of generated SrCO_3 is low.

[0020]When [according to claim 4] a lithium containing transition metal oxide is $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ (however either $\text{M}=\text{Co}$ or Al or Mn or B is used and referred to as $0 < x < 0.3$) like it is possible to obtain high capacity. When the solid solution which the crystal structure of the charging state used as other elements a part of LiNiO_2 which is unstable and has many gas yields at the time of elevated-temperature neglect and its nickel element and was replaced by either Co or Al or Mn or B is used for positive active material the effect of this invention is acquired.

[0021]

[Example] Hereafter an example describes this invention in detail.

[0022](Example 1) The section notch perspective view of the cylindrical shape cell used by this example the conventional example and the comparative example is shown in drawing 1. In drawing 1 the negative electrode plate with which 1 attached the negative electrode lead board 2 and 3 are the anode boards furnished with the positive electrode lead board 4. The negative electrode plate 1 and the anode board 3 are stored in the cell case 7 which serves as a negative pole terminal in the state where the electric insulating plate 6 has been arranged for the group of electrode spirally wound via the separator 5 to the upper and lower sides. The upper limb of the cell case 7 is sealed via the insulating packing 8 with the obturation board 9 which served as the positive pole terminal which provided *****. The inside of the obturation board 9 is designed the flow of a positive pole terminal and the positive electrode lead board 4 lost and intercept the current from the outside if inter cell pressure exceeds 10 kg/cm^2 at 20 **. Hereafter the manufacturing method of an anode board and a negative electrode plate etc. are explained in detail.

[0023] $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was used for positive active material. First weighing of nickel hydroxide cobalt hydroxide and the lithium hydroxide was carried out so that the atomic ratio of nickel:Co:Li might be set to 0.8:0.2:1.0 and it fully mixed with the ball mill. And this mixture was put into the crucible made from alumina and heat treatment of 10 hours was performed at 750 °C into oxygen. And after natural air cooling grinding and a classification were performed and it was considered as positive-active-material powder with a mean particle diameter of about 10 micrometers. Artificial-graphite powder 6 weight section was added to this active material 100 weight section the solution which dissolved the polyvinylidene fluoride (henceforth PVDF) as a binder in this mixture at the solvent of N-methyl pyrrolidone (henceforth NMP) was kneaded and it was made paste state. The quantity of added PVDF was prepared so that it might become four weight sections to active material 100 weight section. Subsequently coating of this paste was carried out to both sides of aluminium foil and after desiccation it rolled and was considered as an anode board 0.14 mm in thickness 37 mm in width and 380 mm in length. In production of an anode board the process of a kneading series or subsequent ones was performed in dry air.

[0024] What heat-treated and graphitized the mesophase microsphere with a mean particle diameter of 6.0 micrometers at 2800 °C was used for the negative electrode. Styrene / butadiene rubber 3 weight section as a binder was mixed to this graphitization mesophase 100 weight section carboxymethyl cellulose solution was added and kneaded and it was made paste state. And coating of this paste was carried out to both sides of copper foil and after desiccation it rolled and was considered as a negative electrode plate 0.20 mm in thickness 39 mm in width and 420 mm in length.

[0025] And the lead board was attached to the anode board and the negative electrode plate respectively and it wound spirally via a separator 0.025 mm in thickness 45 mm in width and 1000 mm in length and stored to a cell case 17.0 mm in diameter and 50 mm in height.

[0026] Then although it was an oxide to add the solution which dissolved PVDF as a binder for SrO with a mean particle diameter of about 8 micrometers in the solvent of NMP by the same method as production of an anode board was kneaded and it was made paste state. Coating of this paste was carried out to one side of aluminium foil after drying and rolling it pierced in a circle 8 mm in diameter and the aluminium foil side was welded [of the obturation board]. The thickness of the oxide layer was 0.08 mm including the thickness of aluminium foil. The fill ration of SrO was taken as 0.1 millimols to the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ 1 g which is positive active material.

[0027] What dissolved 1 mol/l. LiPF_6 in the solvent which mixed ethylene carbonate (henceforth EC) and dimethyl carbonate (henceforth DMC) by the volume ratio of 20:80 as an electrolyte was poured in the electrolysis solution. It was made not to contact the oxide layer which the electrolysis solution has arranged at the obturation board pars basilaris ossis occipitalis in that case. And after the electrolysis solution was fully absorbed by the group of electrode the cell was obturated it was considered as the completion cell and 20 cells were produced as a cell of Example 1.

[0028] (Conventional example) Except it the cell was produced completely like Example 1 and 20 cells were produced as a cell of a conventional example without having arranged the SrO oxide in a fuel cell subsystem.

[0029] (Comparative example) Tales doses of SrO powder to Example 1 has not been

arranged at the pars basilaris ossis occipitalis of an obturation board but it added in the fuel cell subsystem in the state where it mixed into the anode beforehand. Except adding SrO in this anode the cell was produced completely like Example 1 and 20 cells were produced as a cell of a comparative example.

[0030] And the charge and discharge test of the cell of these Examples 1 a conventional example and a comparative example was done. Charge was considered as constant current voltage charge and it charged to 4.2V by 630-mA constant current and after 4.2V attainment is changed into constant potential charge and charge ended in 2 hours. Discharge performed 900-mA constant current discharge and set discharge final voltage to 2.5V. Capacity of 5 cycle and 3 cycle eye was made into initial capacity for such charge and discharge under the environment of 20 °C. And the cell of the charging state was neglected to an 85 °C thermostat for 15 hours. It returned under the environment of 20 °C after that and the flow of the cell was measured. Then about the cell with a flow charge and discharge were performed again and it was considered as the capacity after neglecting the capacity of 3 cycle eye. Since the security apparatus established in the obturation board 9 operated and the flow between an anode and a negative electrode was lost when inter cell pressure exceeded about 10 kg/cm² the rate in which the security apparatus operated by elevated-temperature neglect was searched for. The result was shown in Table 1 with the average value of initial capacity and the capacity after neglect.

[0031]

[Table 1]

[0032] It measured about the cell by which the security apparatus did not operate about the cell capacity after elevated-temperature neglect. By the cell of Example 1 all the cells have a flow even after elevated-temperature neglect and it is shown that the security apparatus is not operating. That is when SrO which formed the gas emitted at the time of elevated-temperature neglect in the inside absorbed inter cell pressure is considered to have fitted below in a predetermined value. The cell capacity after elevated-temperature neglect is also as large as 938mAh and it turns out that the resultant of SrO has not had an adverse effect on a battery characteristic. On the other hand by the cell of the conventional example by elevated-temperature neglect the security apparatus is operating with the rise of inter cell pressure and 15 cells have lost the function as a cell. 14 cells in which the cell of a comparative example is also almost the same brought a result in which the security apparatus operates. Cell capacity is also in the tendency which becomes a little small and is not preferred. In adding SrO in an anode and mixing from the above thing in order to acquire the effect of this invention the purpose cannot be attained but it turns out that it is important to arrange in a fuel cell subsystem so that direct contact may not be carried out to an electrode and an electrolysis solution.

[0033] The cell of Example 1 and the same cell were produced ten cells independently and the overcharge examination was done by the constant current of 1A. The security apparatus operated 18 minutes - 20 minutes afterward and any cell intercepted the current from the outside. Ignition of a cell burst white smoke etc. were not seen but battery surface temperature was about 50 °C. That is even if SrO exists in a fuel cell subsystem the gas absorption at the time of overcharge has not happened or it is expected that the speed is slow and it turns out that this invention is not what spoils the safety at the time of

overcharge.

[0034] (Example 2) BaO was used instead of SrO as an oxide added in the cell of Example 1 the cell which added the addition at a rate shown in Table 2 to 1 g of positive active material was produced and it was considered as the cell A the cell B the cell C the cell D the cell E and the cell F respectively. Charge and discharge were performed like the cell of Example 1 and elevated-temperature neglect of these cells was carried out by the charging state. The flow of the subsequent cell was measured and the result was shown in Table 2.

[0035]

[Table 2]

[0036] By the cell B the cell C the cell D and the cell E the security apparatus does not operate but the effect of this invention is acquired by each. However by the cell A with as few additions as [0.03 millimols] the security apparatus of the more than cell of about half one is operating and it turns out that control of inter cell pressure is insufficient. [0037] The cell on which the security apparatus operated in part also by the cell F with most additions as 0.25 millimols on the other hand was seen. Since the volume of added BaO became large the volume of voids in a cell becomes extremely small and this is considered that the direction of the climbing speed of inter cell pressure became quick and the security apparatus has operated rather than the gas absorption reaction. From these results it can be said that it is important that they are 0.04 millimols - 0.20 millimol per 1 g of positive active material as a quantity of the oxide to add.

[0038] Although $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was used for positive active material in Example 1 and Example 2 the same effect was acquired also when the solid solution and LiCoO_2 which began LiNiO_2 and replaced some nickel by aluminum Mn or B as other elements and LiMn_2O_4 were used. This invention can apply a lithium containing transition metal oxide to the nonaqueous electrolyte secondary battery used for the anode.

[0039] Although what graphitized the mesophase microsphere was used as a negative electrode when what other carbon materials for example artificial graphite corks and carbon fiber etc. carry out occlusion of the lithium such as a metallic oxide or they may emit a lithium alloy and a lithium metal are used lithium can be applied to the nonaqueous electrolyte secondary battery used as the active material.

[0040] The same effect was acquired although SrO or BaO was used as an oxide to add and there was a difference of some of cell capacitance characteristics also when MgO or CaO which is other oxides was used.

[0041] Although it is an electrolyte solution and the mixed solvent of EC and DMC was used for the solvent in this example as other solvents cyclic carbonates such as propylene carbonate and butylene carbonate. Publicly known things such as ethers such as chain carbonates such as diethyl carbonate and ethyl methyl carbonate 1,2-dimethoxyethane and 2-methyltetrahydrofuran are all independent or it is usable as a mixed solvent. It is usable in publicly known things such as LiBF_4 and LiClO_4 also about a solute.

[0042]

[Effect of the Invention] As mentioned above according to this invention when a battery characteristic is satisfied and a cell is neglected by the elevated temperature in a charging state the rise of inter cell pressure is controlled and the advantageous effect of not making

the function as a cell lose is acquired.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The section notch perspective view of the cylindrical shape cell used by this example the conventional example and the comparative example

[Description of Notations]

- 1 Negative electrode plate
 - 2 Negative electrode lead board
 - 3 Anode board
 - 4 Positive electrode lead board
 - 5 Separator
 - 6 Electric insulating plate
 - 7 Cell case
 - 8 Insulating packing
 - 9 Obturation board
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